Structural Characterization of Coal Oils by Proton and Carbon-13 Nuclear Magnetic Resonance

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Introduction

The technique of structural analysis based on proton NMR and elemental analysis has been applied to heavy oils derived from coal and petroleum[1-3]. This approach utilizes the hydrogen types to determine information about the carbon skeleton. Friedel and Retcofsky have applied ^{13}C NMR to coal-derived products to obtain structural information directly[4]. The new technique of pulse Fourier-transform (PFT) spectroscopy has helped overcome the problem of low sensitivity and proton decoupling has simplified the spectra, making ^{13}C NMR more suitable for studies of heavy oils. Structural analysis is still limited by difficulties in making quantitative measurements and in assigning absorption to various types of carbons. Combinations of ^{1}H and ^{13}C NMR have been used to study petroleum liquids[5,6]. More recently PFT ^{13}C NMR has been applied to coal liquids[7,8]. In this study, ^{1}H and ^{13}C NMR are used for the structural characterization of heavy oils derived from coal by catalytic hydrogenation.

Experimental

Hiawatha, Utah coal (45% V.M., d.a.f.b.) was impregnated with 6% by weight Zn as $ZnCl_2$ and hydrogenated in an entrained-flow reactor at 950°F and 1800 psi H_2. The heavy oil fraction was extracted with 10% NaOH and 15% H_2SO_4 and separated into a hexane-soluble oil and an asphaltene fraction by extractions. The hexane-soluble oil was separated into saturate and aromatic fractions by liquid chromatography using a silica gel column. The saturate oil, aromatic oil and asphaltene fractions were separated by size by gel permeation chromatography (GPC) using crosslinked polystyrene gels of pore sizes appropriate to each sample. Neighboring GPC fractions were combined to obtain samples of suitable size. The GPC separation and the samples chosen for analysis are shown in Figure 1.

NMR spectra were measured in d-chloroform using tetramethyl silane as a reference material. A Varian Associates XL-100 FTNMR spectrometer operating at 25.16 MH_z and 0.4 - 0.8 second pulse interval time for ^{13}C NMR and 100 MH_z for ^{1}H NMR was used to obtain spectra. Typical spectra are shown in Figures 2-4.

Results and Discussion

The GPC results shown in Figure 1 are in agreement with molecular weight measurements for the fractions measured by vapor pressure osmometry. The molecular weights of the asphaltenes varied from 1380 for the fraction eluted at lowest elution volume to 410 for the fraction eluted last. The aromatic oil fractions have molecular weights in the range 250-610. The H/C ratios decrease from 0.94 to 0.83 for the asphaltene fractions and from 1.51 to 0.85 for the aromatic oil fractions with increasing elution volume.

The NMR spectra of the saturate oil fractions in Figure 2 show a typical pattern of a long chain aliphatic compound. The ^{13}C spectra show resonance lines at 14, 23, 32, 29 and 29.5 ppm corresponding to the α, β, γ, σ and ε carbons respectively of n-paraffins. The average chain length was calculated from the

ratio of peak areas for the various carbon types assuming the structure of a normal paraffin. The results are shown in Table 1, with the calculated amount of n-paraffinic structure and the number of carbons estimated from gas chromatography results. The chain length calculated from ^{13}C NMR is greater than that obtained from gas chromatography. This is attributed to branching near the end of the carbon chain which invalidates the n-paraffin model. The low-molecular weight saturate fractions contains considerable isoparaffins.

The NMR spectra of aromatic oil fractions in Figure 3 indicate a gradual change in structural properties with elution volume. The spectra of larger molecules (eluted at smaller volumes) indicate long alkyl groups attached to small aromatic ring systems. The length of the alkyl substituents was estimated from the intensities of resonance peaks with chemical shifts equivalent to n-paraffin carbons. For fraction O-1, 57% of the saturated carbons are in such alkyl groups and the average length is 28 carbons. For fraction O-2, the corresponding figures are 35% and 10 carbons. With increasing elution volume, the spectra progressively changes to a complex broad spectra. The spectra for fraction O-7 indicates a higher fraction of aromaticity, fa, and that almost all hydrogens are bound to aromatic carbons and carbons α to aromatic rings. Examination of the spectra in Figure 4 shows a similar trend for the asphaltene fractions.

The chemical shift assignments of Bartle, et.al.[7] were used to determine the carbons α to aromatic rings, $C\alpha$, and those β or further, Co, from the ^{13}C NMR spectra. From ^{1}H NMR spectra, protons bound to each type of carbon, $H\alpha$ and Ho respectively, were calculated. Values of Ho/Co (Y) for aromatic oil fractions are reasonable, but values of $H\alpha/C\alpha$ (X) indicate a possible error in the assignments of chemical shifts.

The fractions of aromatic carbon are plotted versus elution volume in Figure 5 as determined from the ^{13}C NMR spectra and by structural analysis using ^{1}H NMR spectra[2]. The structural analysis approach assumes that X=Y=2. The ^{13}C NMR spectra is complicated by the long relaxation times of aromatic carbons that are not bound to hydrogens. These carbons generally show chemical shifts downfield from 129 ppm while aromatic carbons bound to hydrogens, Cah, show chemical shifts upfield from 129 ppm[7,8]. Cah can be equated to the aromatic hydrogens and the ratio of aliphatic hydrogen to carbon is given by equation 1.

$$Hal/Cal = Cah/Cal \cdot Hal/Ha \qquad (1)$$

The ratios on the right hand side of equation 1 can be obtained from the ^{13}C NMR spectra, assuming the division at 129 ppm and from ^{1}H NMR. Values of Hal/Cal are listed in Table 2. Figure 6 shows the value of structural parameters calculated by the Brown-Ladner equations[2] for X=Y=2 and X=Y=Hal/Cal, using the results in Table 2.

References

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Table 1
Structure of Saturate Fractions

Fraction	^{13}C NMR		Gas Chromatography
	Carbon Number	% Normal Paraffin	Carbon Number
1-P	50-60	67	33
2-P	34	86	27
3-P	23-28	54	22

Table 2
Aliphatic Carbon to Hydrogen Ratio

Fraction Number		1	2	3	4	5	6	7
Hal/Cal	Aromatic Oil	2.0	2.1	2.1	4.5	2.2	2.4	2.6
	Asphaltene	1.6	2.3	1.9	1.8	2.4	2.6	2.7

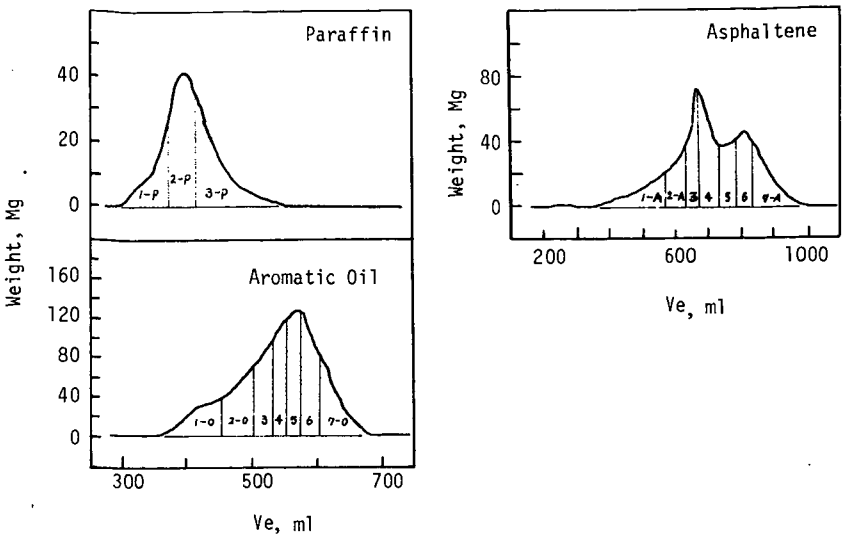

Figure 1. GPC Elution Curves

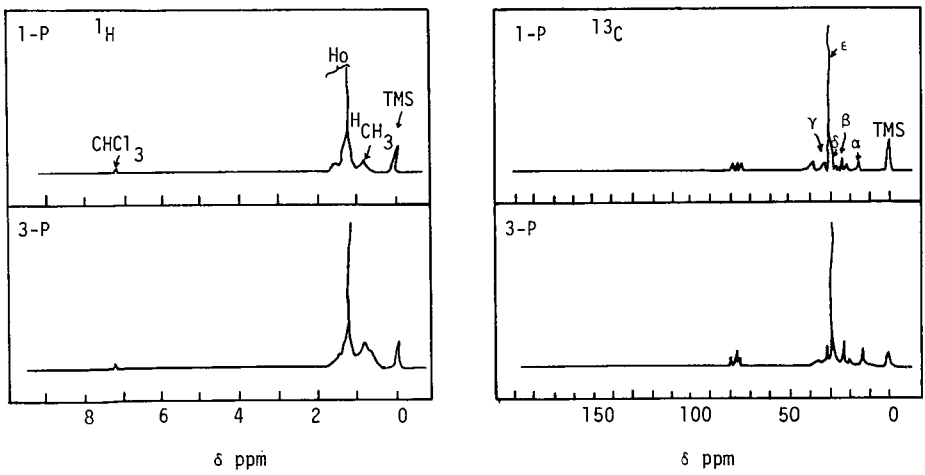

Figure 2. ^1H and ^{13}C NMR spectra of Paraffin Fractions

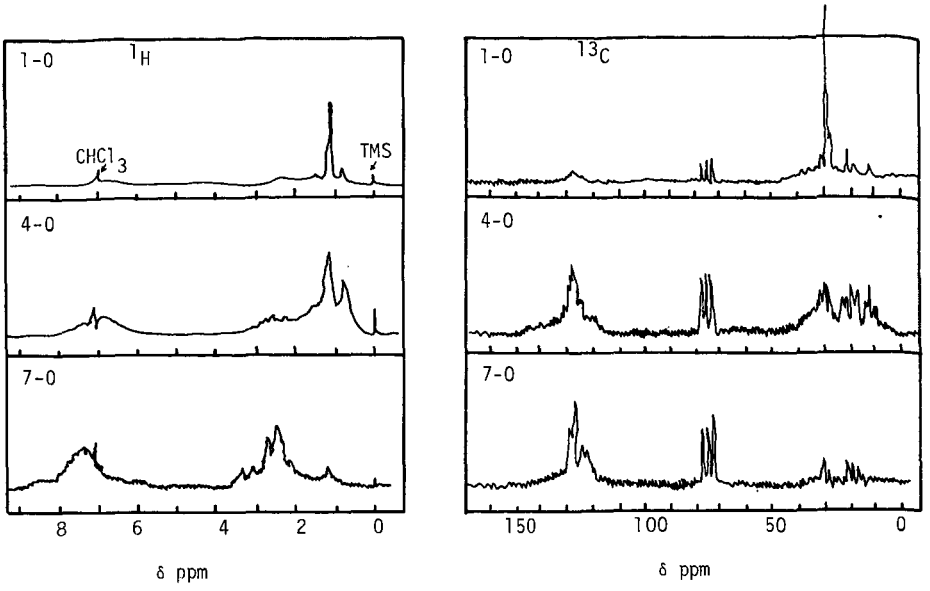

Figure 3. ^{1}H and ^{13}C NMR Spectra of Aromatic Oil Fractions

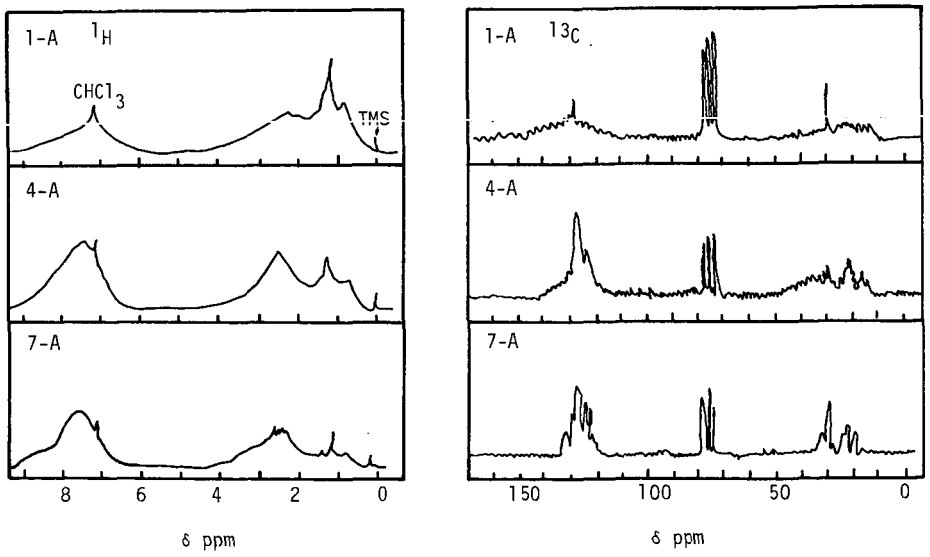

Figure 4. ^{1}H and ^{13}C NMR Spectra of Asphaltene Fractions

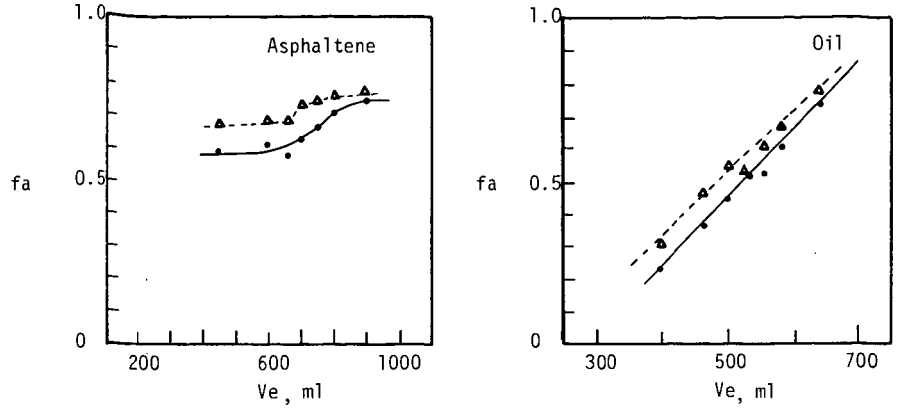

Figure 5. Carbon aromaticity: solid line from ^{13}C NMR, dashed line from ^{1}H NMR.

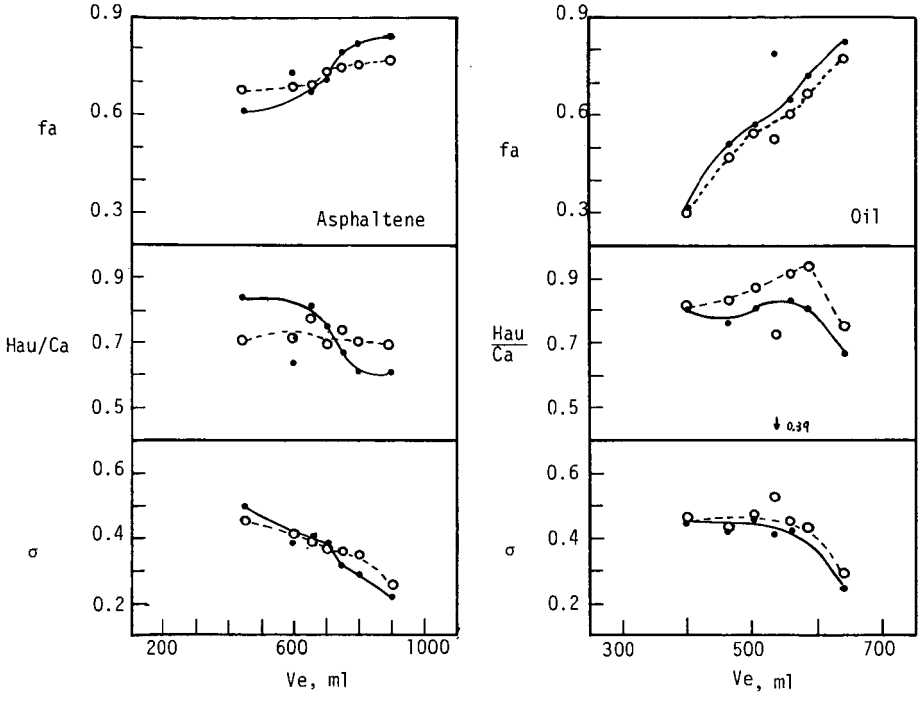

Figure 6. Structural Parameters: solid line from ^{13}C, dashed line from ^{1}H NMR